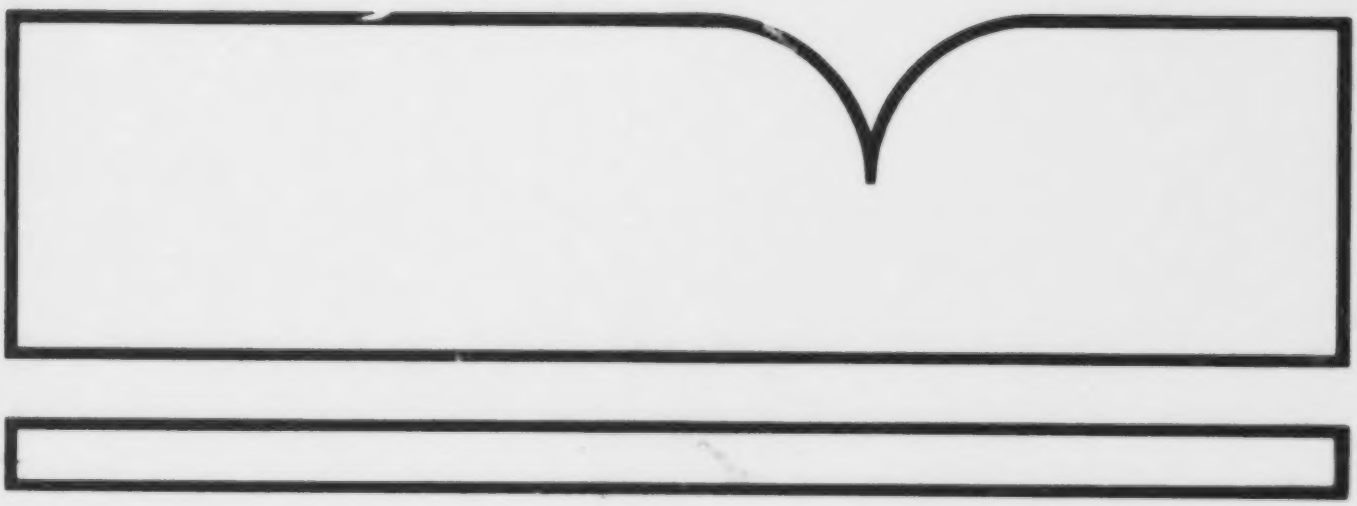
PB82-156068

The Determination of Benomyl and Carbendazim in Industrial and Municipal Wastewater: Method 631

(U.S.) Environmental Monitoring and Support Lab.-Cincinnati, OH

Feb 82



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PB82-156068

THE DETERMINATION OF BENOMYL AND CARBENDAZIM IN INDUSTRIAL AND MUNICIPAL WASTEWATER

Method 631

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January 1982

ENVIRONMENTAL MONITORING AND SUPPORT LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/4-82-012 m	REPORT	PB82 156068

4. TITLE AND SUBTITLE	5. REPORT DATE
The Determination of Benomyl and Carbendazim in Industrial and Municipal Wastewater Method 631	February 1982
	6. PERFORMING ORGANIZATION CODE 033008
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Thomas A. Pressley and James E. Longbottom	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Environmental Monitoring and Support Lab - Cincinnati Office of Research and Development U. S. Environmental Protection Agency Cincinnati, Ohio 45268	10. PROGRAM ELEMENT NO. ABEB1C
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Same as Above	13. TYPE OF REPORT AND PERIOD COVERED Final
	14. SPONSORING AGENCY CODE EPA/600/6

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This is a high performance liquid chromatographic (HPLC) method appliicable to the determination of carbendazim and benomyl in municipal and industrial discharges as provided under 40CFR 136.1. A sample is acidified to hydrolyze benomyl to carbendazim. The total carbendazim is extracted with methylene chloride using a separatory funnel. The extract is exchanged to methanol during concentration. HPLC conditions are described which permit measurement with an ultraviolet detector.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES
Release to Public	Unclassified	19
	20. SECURITY CLASS (This page) Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

THE DETERMINATION OF BENOMYL AND CARBENDAZIM
IN INDUSTRIAL AND MUNICIPAL WASTEWATER

METHOD 631

1. Scope and Application

1.1 This method covers the determination of benomyl and carbendazim. The following parameters can be determined by this method:

Parameter	STORET No.	CAS No.
Benomyl	--	17804-35-2
Carbendazim	--	10605-21-7

1.2 Benomyl cannot be determined directly by this method. Benomyl is hydrolyzed to carbendazim, and both compounds are measured and reported as carbendazim.

1.3 This is a high performance liquid chromatographic (HPLC) method applicable to the determination of the compounds listed above in industrial and municipal discharges as provided under 40 CFR 136.1. Any modification of this method beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.

1.4 The method detection limit (MDL, defined in Section 15) for each parameter is 8.7 µg/L. The MDL for a specific wastewater may differ from those listed, depending upon the nature of interferences in the sample matrix.

1.5 This method is restricted to use by or under the supervision of analysts experienced in the use of liquid chromatography and in the interpretation of liquid chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedure described in Section 8.2.

1.6 When this method is used to analyze unfamiliar samples for either of the compounds above, compound identifications should be supported by at least one additional qualitative technique.

2. Summary of Method

2.1 A measured volume of sample, approximately 1 liter, is acidified if necessary to hydrolyze benomyl to carbendazim. The total carbendazim is extracted with methylene chloride using a separatory funnel. The extract is dried and exchanged to methanol during concentration to a volume of 10 mL or less. HPLC conditions are described which permit the separation and measurement of total carbendazim in the extract by HPLC with a UV detector.[1,2]

3. Interferences

3.1 Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines in liquid chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks as described in Section 8.5.

3.1.1 Glassware must be scrupulously cleaned.[3] Clean all glassware as soon as possible after use by thoroughly rinsing with the last solvent used in it. Follow by washing with hot water and detergent and thorough rinsing with tap and reagent water. Drain dry, and heat in an oven or muffle furnace at 400°C for 15 to 30 min. Do not heat volumetric ware. Thermally stable materials such as PCBs, might not be eliminated by this treatment. Thorough rinsing with acetone and pesticide quality hexane may be substituted for the heating. After drying and cooling, seal and store glassware in a clean environment to prevent any accumulation of dust or other contaminants. Store inverted or capped with aluminum foil.

3.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

3.2 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the industrial complex or municipality sampled. Unique samples may require cleanup approaches to achieve the MDL listed in Section 1.

4. Safety

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined; however, each chemical compound must be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible

for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available and have been identified [4-6] for the information of the analyst.

5. Apparatus and Materials

5.1 Sampling equipment, for discrete or composite sampling.

5.1.1 Grab sample bottle - Amber borosilicate or flint glass, 1-liter or 1-quart volume, fitted with screw caps lined with TFE-fluorocarbon. Aluminum foil may be substituted for TFE if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container and cap liner must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

5.1.2 Automatic sampler (optional) - Must incorporate glass sample containers for the collection of a minimum of 250 mL. Sample containers must be kept refrigerated at 4°C and protected from light during compositing. If the sampler uses a peristaltic pump, a minimum length of compressible silicone rubber tubing may be used. Before use, however, the compressible tubing must be thoroughly rinsed with methanol, followed by repeated rinsings with reagent water to minimize the potential for contamination of the sample. An integrating flow meter is required to collect flow proportional composites.

5.2 Glassware (All specifications are suggested. Catalog numbers are included for illustration only.)

5.2.1 Separatory funnel - 250-mL, with TFE-fluorocarbon stopcock, ground glass or TFE stopper.

5.2.2 Drying column - Chromatographic column 400 mm long x 19 mm ID with coarse fritted disc.

5.2.3 Concentrator tube, Kuderna-Danish - 10-mL, graduated (Kontes K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

5.2.4 Evaporative flask, Kuderna-Danish - 500-mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

5.2.5 Snyder column, Kuderna-Danish - three-ball macro (Kontes K-503000-0121 or equivalent).

5.2.6 Vials - Amber glass, 10 to 15 mL capacity with TFE-fluorocarbon lined screw cap.

5.3 Boiling chips - approximately 10/40 mesh. Heat at 400°C for 30 min or Soxhlet extract with methylene chloride.

5.4 Water bath - Heated, with concentric ring cover, capable of temperature control (± 2°C). The bath should be used in a hood.

5.5 Balance - Analytical, capable of accurately weighing to the nearest 0.0001 g.

5.6 Liquid chromatograph - High performance analytical system complete with high pressure syringes or sample injection loop, analytical columns, detector and strip chart recorder. A guard column is recommended for all applications.

5.6.1 Column - 30 cm long x 4 mm ID stainless steel, packed with μ Bondapak C_{18} (10 μm) or equivalent. This column was used to develop the method performance statements in Section 14. Alternative columns may be used in accordance with the provisions described in Section 12.1.

5.6.2 Detector - Ultraviolet, 254 nm. This detector has proven effective in the analysis of wastewaters and was used to develop the method performance statements in Section 14. Alternative detectors may be used in accordance with the provisions described in Section 12.1.

6. Reagents

6.1 Reagent water - Reagent water is defined as a water in which an interferent is not observed at the method detection limit of each parameter of interest.

6.2 Methylene chloride, methanol - Pesticide quality or equivalent.

6.3 Sodium sulfate - (ACS) Granular, anhydrous. Heat treat in a shallow tray at 400°C for a minimum of 4 h to remove phthalates and other interfering organic substances. Alternatively, heat 16 h at 450-500°C in a shallow tray or Soxhlet extract with methylene chloride for 48 h.

6.4 Sodium hydroxide solution (10N) - Dissolve 40g NaOH in reagent water and dilute to 100 mL.

6.5 Sulfuric acid solution (1+1) - Slowly add 50 mL H_2SO_4 (sp. gr. 1.84) to 50 mL of reagent water.

6.6 Mobile phase - Methanol/water (1+1). Mix equal volumes of HPLC/UV quality methanol and reagent water.

6.7 Stock standard solution (1.00 µg/µL) - The stock standard solution may be prepared from a pure standard material or purchased as a certified solution.

6.7.1 Prepare the stock standard solution by accurately weighing approximately 0.0100 g of pure carbendazim. Dissolve the material in HPLC/UV quality methanol and dilute to volume in a 10-mL volumetric flask. Larger volumes may be used at the convenience of the analyst. If compound purity is certified at 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

6.7.2 Transfer the stock standard solution into a TFE-fluorocarbon-sealed screw cap vial. Store at 4°C and protect from light. Frequently check stock standard solutions for signs of degradation or evaporation, especially just prior to preparing calibration standards from them.

6.6.3 The stock standard solution must be replaced after six months or sooner if comparison with a check standard indicates a problem.

7. Calibration

7.1 Establish HPLC operating parameters equivalent to those indicated in Table 1. The HPLC system may be calibrated using either the external standard technique (Section 7.2) or the internal standard technique (Section 7.3).

7.2 External standard calibration procedure:

7.2.1 Prepare calibration standards at a minimum of three concentration levels by adding accurately measured volumes of carbendazim stock standard to volumetric flasks and diluting to volume with methanol. One of the external standards should be representative of a concentration near, but above, the method detection limit. The other concentrations should correspond to the range of concentrations expected in the sample concentrates or should define the working range of the detector.

7.2.2 Using injections of 10 µL of each calibration standard, tabulate peak height or area responses against the mass injected. The results can be used to prepare a calibration curve for carbendazim. Alternatively, the ratio of the response to the mass injected, defined as the calibration factor (CF), may be calculated for carbendazim at each standard concentration. If the relative standard deviation

of the calibration factor is less than 10% over the working range, the average calibration factor can be used in place of a calibration curve.

7.2.3 The working calibration curve or calibration factor must be verified on each working shift by the measurement of one or more calibration standards. If the response for any parameter varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve or calibration factor must be prepared.

7.3 Internal standard calibration procedure. To use this approach, the analyst must select an internal standard similar to carbendazim in analytical behavior. The analyst must further demonstrate that the measurement of the internal standard is not affected by method or matrix interferences. Due to these limitations, no internal standard applicable to all samples can be suggested.

7.3.1 Prepare calibration standards at a minimum of three concentration levels of carbendazim by adding volumes of stock standard to volumetric flasks. To each calibration standard, add a known constant amount of internal standard, and dilute to volume with methanol. One of the standards should be representative of a concentration near, but above, the method detection limit. The other concentrations should correspond to the range of concentrations expected in the sample concentrates, or should define the working range of the detector.

7.3.2 Using injections of 10 µL of each calibration standard, tabulate the peak height or area responses against the concentration for each compound and internal standard. Calculate response factors (RF) for each compound as follows:

$$RF = (A_s C_{is})/(A_{is} C_s)$$

where:

A_s = Response for carbendazim.
A_{is} = Response for the internal standard.
C_{is} = Concentration of the internal standard in µg/L.
C_s = Concentration of carbendazim in µg/L.

If the RF value over the working range is constant, less than 10% relative standard deviation, the RF can be assumed to be invariant and the average RF may be used for calculations. Alternatively, the results may be used to plot a calibration curve of response ratios, A_s/A_{is} against RF.

7.3.3 The working calibration curve or RF must be verified on each working shift by the measurement of one or more calibration

standards. If the response for carbendazim varies from the predicted response by more than ±10%, the test must be repeated using a fresh calibration standard. Alternatively, a new calibration curve must be prepared.

7.4 Before using any cleanup procedure, the analyst must process a series of calibration standards through the procedure to validate elution patterns and the absence of interference from the reagents.

8. Quality Control

8.1 Each laboratory using this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.1.1 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 8.2.

8.1.2 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 8.2.

8.1.3 The laboratory must spike and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. This procedure is described in Section 8.4.

8.2 To establish the ability to generate acceptable accuracy and precision, the analyst must perform the following operations.

8.2.1 Select a representative spike concentration for each compound to be measured. Using stock standards, prepare a quality control check sample concentrate of either benomyl or carbendazim in methanol 1000 times more concentrated than the selected concentrations.

8.2.2 Using a pipet, add 1.00 mL of the check sample concentrate to each of a minimum of four 1000-mL aliquots of reagent water. A representative wastewater may be used in place of the reagent water, but one or more additional aliquots must be analyzed to determine background levels, and the spike level must exceed twice the background level for the test to be valid. Analyze the aliquots according to the method beginning in Section 10.

8.2.3 Calculate the average percent recovery (R), and the standard deviation of the percent recovery (s), for the results. Wastewater background corrections must be made before R and s calculations are performed.

8.2.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values calculated in Section 8.2.3. If the data are not comparable, review potential problem areas and repeat the test.

8.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration and parameter being measured.

8.3.1 Calculate upper and lower control limits for method performance as follows:

$$\text{Upper Control Limit (UCL)} = R + 3s$$
$$\text{Lower Control Limit (LCL)} = R - 3s$$

where R and s are calculated as in Section 8.2.3. The UCL and LCL can be used to construct control charts[7] that are useful in observing trends in performance.

8.3.2 The laboratory must develop and maintain separate accuracy statements of laboratory performance for wastewater samples. An accuracy statement for the method is defined as $R \pm s$. The accuracy statement should be developed by the analysis of four aliquots of wastewater as described in Section 8.2.2, followed by the calculation of R and s. Alternatively, the analyst may use four wastewater data points gathered through the requirement for continuing quality control in Section 8.4. The accuracy statements should be updated regularly.[7]

8.4 The laboratory is required to collect in duplicate a portion of their samples to monitor spike recoveries. The frequency of spiked sample analysis must be at least 10% of all samples or one spiked sample per month, whichever is greater. One aliquot of the sample must be spiked and analyzed as described in Section 8.2. If the recovery for benomyl or carbendazim does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 13.3. The laboratory should monitor the frequency of data so qualified to ensure that it remains at or below 5%.

8.5 Before processing any samples, the analyst must demonstrate through the analysis of a 1-liter aliquot of reagent water that all glassware and reagent interferences are under control. Each time

a set of samples is extracted or there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

8.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak on the chromatogram as carbendazim, confirmatory techniques such as chromatography with a dissimilar column, or ratio of absorbance at two or more wavelengths may be used. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance evaluation studies.

9. Sample Collection, Preservation, and Handling

9.1 Grab samples must be collected in glass containers. Conventional sampling practices[8] should be followed; however, the bottle must not be prerinsed with sample before collection. Composite samples should be collected in refrigerated glass containers in accordance with the requirements of the program. Automatic sampling equipment must be as free as possible of plastic and other potential sources of contamination.

9.2 The samples must be iced or refrigerated at 4°C from the time of collection until extraction.

9.3 All samples must be extracted within seven days and completely analyzed within 40 days of extraction.

10. Sample Extraction

10.1 Using a 250-mL graduated cylinder, measure 150 mL of well-mixed sample into a 250-mL Erlenmeyer flask. If benomyl is a potentiality in the sample, continue with Section 10.2. If only carbendazim is to be measured, proceed directly to Section 10.3.

10.2 Carefully add 2 mL of 1+1 sulfuric acid and a TFE-fluorocarbon covered magnetic stirring bar to the sample. Check the sample with wide-range pH paper to insure that the pH is less than 1.0. Stir at room temperature for 16 to 24 h.

10.3 Adjust the sample pH to within the range of 6 to 8 with sodium hydroxide. Pour the entire sample into a 250-mL separatory funnel.

10.4 Add 60 mL methylene chloride to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting to release excess pressure. Allow the organic layer to separate from the water phase for a minimum of 10 min. If the emulsion interface

between layers is more than one third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. The optimum technique depends upon the sample, but may include stirring, filtration of the emulsion through glass wool, centrifugation, or other physical methods. Collect the methylene chloride extract in a 250-mL Erlenmeyer flask.

10.5 Add a second 60-mL volume of methylene chloride to the separatory funnel and repeat the extraction procedure a second time, combining the extracts in the Erlenmeyer flask. Perform a third extraction in the same manner.

10.6 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10-mL concentrator tube to a 500-mL evaporative flask. Other concentration devices or techniques may be used in place of the K-D if the requirements of Section 8.2 are met.

10.7 Pour the combined extract through a drying column containing about 10 cm of anhydrous sodium sulfate, and collect the extract in the K-D concentrator. Rinse the Erlenmeyer flask and column with 20 to 30 mL of methylene chloride to complete the quantitative transfer.

10.8 Add 1 or 2 clean boiling chips to the evaporative flask and attach a three-ball Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath, 60 to 65°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 min. At the proper rate of distillation, the balls of the column will actively chatter but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.9 Increase the temperature of the hot water bath to 85 to 90°C. Momentarily remove the Snyder column, add 50 mL of methanol and a new boiling chip and reattach the Snyder column. Pour about 1 mL of methanol into the top of the Snyder column and concentrate the solvent extract as before. Elapsed time of concentration should be 5 to 10 min. When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 min.

10.10 Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methanol and adjust the volume to 10 mL. A 5-mL syringe is recommended for this operation. Stopper the concentrator tube and store refrigerated if further processing will not be performed immediately. If the

extracts will be stored longer than two days, they should be transferred to TFE-fluorocarbon-sealed screw-cap vials. Proceed with HPLC analysis.

11. Cleanup and Separation

11.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. If particular circumstances demand the use of a cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of each compound of interest for the cleanup procedure is no less than 85%.

12. Liquid Chromatography

12.1 Table 1 summarizes the recommended operating conditions for the liquid chromatograph. Included in this table are the estimated retention time and method detection limit that can be achieved by this method. An example of the separation achieved by this column is shown in Figure 1. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements of Section 8.2 are met.

12.2 Calibrate the system daily as described in Section 7.

12.3 If the internal standard approach is being used, add the internal standard to sample extracts immediately before injection into the instrument. Mix thoroughly.

12.4 Inject 10 µL of the sample extract. Record the volume injected to the nearest 0.05 µL, and the resulting peak size in area or peak height units.

12.5 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

12.6 If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze.

12.7 If the measurement of the peak response is prevented by the presence of interferences, further cleanup is required.

13. Calculations

13.1 Determine the concentration of carbendazim in the sample.

13.1.1 If the external standard calibration procedure is used, calculate the amount of material injected from the peak response using the calibration curve or calibration factor in Section 7.2.2. The concentration in the sample can be calculated as follows:

$$\text{Concentration, } \mu g/L = \frac{(A)(V_t)}{(V_i)(V_s)}$$

where:

A = Amount of carbendazim injected, in nanograms.
V_i = Volume of extract injected in µL.
V_t = Volume of total extract in µL.
V_s = Volume of water extracted in mL.

13.1.2 If the internal standard calibration procedure was used, calculate the concentration in the sample using the response factor (RF) determined in Section 7.3.2 as follows:

$$\text{Concentration, } \mu g/L = \frac{(A_s)(I_s)}{(A_{is})(RF)(V_o)}$$

where:

A_s = Response for carbendazim.
A_{is} = Response for the internal standard.
I_s = Amount of internal standard added to each extract in µg.
V_o = Volume of water extracted, in liters.

13.2 If the sample was treated to hydrolyze benomyl, report the results as benomyl (measured as carbendazim). If the hydrolysis step was omitted, report results as carbendazim. Report results in micrograms per liter without correction for recovery data. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

13.3 For samples processed as part of a set where the laboratory spiked sample recovery falls outside of the control limits in Section 8.3, data for the affected parameters must be labeled as suspect.

14. Method Performance

14.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero.[9] The MDL concentrations listed in Table 1 were determined by extracting 1000-mL aliquots of reagent water with three 350 mL volumes of methylene chloride.[1]

14.2 In a single laboratory (West Cost Technical Services, Inc.), using reagent water and effluents from publicly owned treatment works

(POTW), the average recoveries presented in Table 2 were obtained.[1] The standard deviations of the percent recoveries of these measurements are also included in Table 2. All results were obtained using the same experimental scale described in Section 14.1.

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TABLE 1

CHROMATOGRAPHIC CONDITIONS AND
METHOD DETECTION LIMITS

Parameter	Retention Time (min)	Method Detection Limit (µg/L)
Benomyl (as carbendazim)	--	25.0
Carbendazim	8.1	8.7

Column conditions: µ Bondapak C_{18} (10 µm) packed in a 30 cm long x 4 mm ID stainless steel column with a mobile phase flow rate of 2.0 mL/min at ambient temperature.
Mobile phase: methanol/water (1+1)

TABLE 2

SINGLE OPERATOR ACCURACY AND PRECISION

Parameter	Sample Type	Number of Replicates	Spike (µg/L)	Average Percent Recovery	Standard Deviation (%)
Benomyl (as carbendazim)	DW	7	51.5	70	15.5
	MW	7	51.5	78	8.8
	MW	7	103	99	6.4
Carbendazim	DW	7	50	106	5.5
	MW	7	50	117	18.5
	MW	7	100	108	11.3

DW = Reagent water
MW = Municipal wastewater

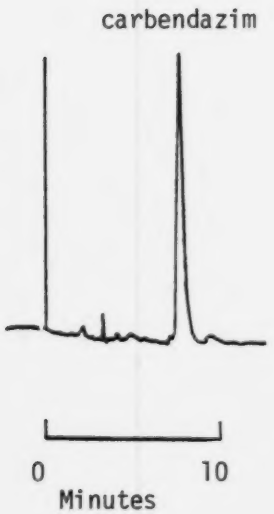

Figure 1. Liquid chromatogram of carbendazim on Column 1. For conditions, see Table 1.